REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
11-06-2015	Final Report	20-Aug-2013 - 19-Aug-2014

4. TITLE AND SUBTITLE

Final Report: Consolidation of Fe16N2 Magnets Using Equal Channel Angular Extrusion

5a. CONTRACT NUMBER
W911NF-13-1-0359

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
611102

6. AUTHORS
S.G. Sankar

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
Advanced Materials Corporation
Advanced Materials Corporation
850 Poplar Street
Pittsburgh, PA 15220 -2828

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)

U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
63585-MS.1

12. DISTRIBUTION AVAILIBILITY STATEMENT

Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES

The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT

ECAE experiments on the Fe16N2 phase materials (containing 3 wt% Mn) showed that:
1. Under the experimental conditions investigated thus far, the best density of the extruded specimens are about 75% of the
X-ray density. Extrusions at temperatures up to ~150 oC do not have any deteriorating effects on the magnetization values
(compared to the powder). However, extrusions at temperatures ~150 oC result in a small change in the intrinsic

15. SUBJECT TERMS

Extrusion, ECAE, Fe16N2, Magnetic Properties, Magnetization, Coercivity, Microstructure

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Suryanarayan Sankar
UU	UU	UU	UU		19b. TELEPHONE NUMBER 412-921-9600

Report Title

Final Report: Consolidation of Fe16N2 Magnets Using Equal Channel Angular Extrusion

ABSTRACT

ECAE experiments on the Fe16N2 phase materials (containing 3 wt% Mn) showed that:
1. Under the experimental conditions investigated thus far, the best density of the extruded specimens are about 75% of the X-ray density. Extrusions at temperatures up to ~150 oC do not have any deteriorating effects on the magnetization values (compared to the powder). However, extrusions at temperatures ~150 oC result in a small change in the intrinsic coercivity.
2. The best saturation induction obtained on the extruded specimen is ~12.5 kG. The potential to enhance these properties is very high with the selection of Fe16N2 powder that is now available at AMC and with more optimized conditions of extrusion.
3. We have performed very limited extrusions. We believe that there are many more variables we need to examine to improve the density and induce crystal and magnetic texture.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 2.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Names of Post Doctorates

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Names of Faculty Supported

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED
Dr. Satoru Simizu	0.10
Mr. Brian Zande	0.20
FTE Equivalent:	**0.30**
Total Number:	**2**

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Technology Transfer

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
06-10-2015	FINAL REPORT	20/08/2013-19/08/2014

4. TITLE AND SUBTITLE

CONSOLIDATION OF Fe-N MAGNETS USING EQUAL CHANNEL ANGULAR EXTRUSION

5a. CONTRACT NUMBER

5b. GRANT NUMBER
W911NF 1310359

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S): S.G. Sankar

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) AND ADDRESS(ES)

Advanced Materials Corporation
850 Poplar Street
Pittsburgh, PA 15220

8. PERFORMING ORGANIZATION REPORT NUMBER

AMCArmy2015A

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U.S. Army
ACC-APG-RTPW911NF
4300 S. Miami Blvd., Durham NC 27703

10. SPONSOR/MONITOR'S ACRONYM(S)
ACC-APG-RTPW911NF

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

UNLIMITED

13. SUPPLEMENTARY NOTES

14. ABSTRACT

ECAE experiments on the $Fe_{16}N_2$ phase materials (containing 3 wt% Mn) showed that:
1. Under the experimental conditions investigated thus far, the best density of the extruded specimens are about 75% of the X-ray density. Extrusions at temperatures up to ~150 ^oC do not have any deteriorating effects on the magnetization values (compared to the powder). However, extrusions at temperatures ~150 ^oC result in a small change in the intrinsic coercivity.
2. The best saturation induction obtained on the extruded specimen is ~12.5 kG. The potential to enhance these properties is very high with the selection of $Fe_{16}N_2$ powder that is now available at AMC and with more optimized conditions of extrusion.
3. We have performed very limited extrusions. We believe that there are many more variables we need to examine to improve the density and induce crystal and magnetic texture.

15. SUBJECT TERMS

EXTRUSION, ECAE, IRON NITRIDE, MAGNETIC PROPERTIES, MAGNETIZATION, COERCIVITY

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			S.G. Sankar
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	NONE	18	19b. TELEPHONE NUMBER *(include area code)* (412) 921 9600

I. INTRODUCTION

Permanent magnets are crucial components in the construction of light-weight, high-efficiency brushless motors, generators and magnetic bearings. They play a prominent role in the civilian and military sectors of our economy. Civilian applications include computer peripherals, wind mill generators, electric vehicles and medical devices. Military applications include army tanks, helicopters, unmanned aerial vehicles, electric vehicles, electric guns, microelectronic devices etc. Enhancement of the magnetic remanence, coercivity and energy product, over a wide operating temperature range are the most desirable goals in permanent magnets development. Further, optimization of processing conditions, examining processing techniques as applicable to the production of permanent magnets, replacing a part or whole of the rare earth metal with other less critical materials and reducing their cost are desirable.

At present, magnets based on the $Nd_2Fe_{14}B$ composition are widely used in almost all the commercial applications while those based on Sm_2Co_{17} are used in a majority of the military applications where thermal stability is a pre-requisite.

A number of potentially useful materials for the fabrication of magnets such as $Fe_{16}N_2$ [1-4] and $Sm_2Fe_{17}N_x$ are thermally sensitive and therefore powders made from them cannot be consolidated to full density through techniques that are commonly employed in the industry such as powder metallurgy and hot deformation. The latter require treatments at high temperatures, typically around 1000 ^oC. In this work, we have explored the potential use of Equal Channel Angular Extrusion (ECAE) to consolidate the $Fe_{16}N_2$ powders [5] to prepare dense bodies at temperatures of 100 and 150 ^oC. ECAE offers the following unique advantages:

1. It ensures the retention of volatile components such as nitrogen in $Fe_{16}N_2$ or in $Sm_2Fe_{17}N_x$ and thus retains their crystal structure which determines their magnetic properties.
2. It prevents the growth of the grains. Powders with nanocrystalline structure do not have a chance of growing into large grains. Thus, they retain some magnetic, electronic and mechanical properties that are unique to nanocrystalline phases such as exchange-coupling.
3. Such a method helps in the formation of bulk structures with nearly 100% density.
4. By repeatedly passing the sample through the ECAE process, grain refinement, modification of grain boundaries, introduction of pinning centers and changes in the defect structures have been shown to develop of some or a selective combination of these modifications can be successfully accomplished in exchange coupled permanent magnets, the potential to enhance the magnetic properties of permanent magnets and create a new technological break-through exists. However, this will require a sustained effort.
5. The ECAE method helps to induce texture and thus promotes crystalline alignment. This feature is very useful in fabricating uniaxial magnets that would increase the magnetization in one crystalline direction and result in magnets with higher magnetic energy product.

II. BACKGROUND

AMC has recently developed a low temperature processing technology to fabricate $Fe_{16}N_2$ powder [6-7]. The process consists of first making nanocrystalline α-iron by reducing iron oxide and then reacting, in-situ, the resultant product with mixtures containing varying amounts of hydrogen, nitrogen and/or helium at temperatures below ~400 ^oC in a fluidized bed reactor[9]. Figure 1 illustrates the formation of the Fe-N phases as a function of the processing conditions. A typical illustration of the variation of the magnetization in relation to the nitriding temperature of α-Fe is shown in Figure 2. Magnetization on a per gram basis of the powder is about 5% higher than that of α-Fe (See Figure 2). The saturation magnetization of the powder showed that it is nearly 240 emu/g., which is much higher than that of α-Fe. The intrinsic coercivity of this powder is nearly 1,000 Oe.

In more recent work at AMC with the support obtained from this grant as well as a small contract from ARPA-E, we have successfully synthesized pure $Fe_{16}N_2$ nanocrystalline powder with magnetization of >200 emu/g. at an external field of ~16 kOe, a saturation magnetization of ~240 emu/g. and an intrinsic coercivity of ~2,300 Oe. This is the first instance where anyone has produced $Fe_{16}N_2$ powder with both high saturation magnetization and a high coercivity [8-11].

AMC has developed a reliable, reproducible and patented technique to produce $Fe_{16}N_2$ nanocrystalline powders. The challenge addressed in this work was to consolidate these powders into dense bodies for use in practical applications. However, the presence of a phase transition at ~240 ^oC in $Fe_{16}N_2$, where nitrogen atoms begin to reorganize and form a mixture of Fe_4N and α-Fe, imposes a severe restriction on the consolidation of this material using conventional high temperature powder metallurgical techniques that are typically employed in magnetic materials such as Sm-Co and NdFeB.

ECAE is one of the few techniques that may be useful to consolidate the $Fe_{16}N_2$ powders due to the fact that this technique may be performed even at near room temperature to densify powders. Published literature on materials using ECAE indicate that it has been used to densify powders of copper and magnesium alloys.

III. WORK COMPLETED UNDER THIS CONTRACT

A. Synthesis of $Fe_{16}N_2$ Powder

$Fe_{16}N_2$ powder was made by initially preparing the oxy-hydroxide, then decomposing into an oxide, reducing the product in flowing hydrogen to metallic iron in a fluidized bed reactor at temperatures between 280 and 400 ^oC, followed by nitriding the metallic iron powder thus formed in a flowing nitrogen (and ammonia) gas at temperatures between 140 and 180 ^oC for several hours. In some experiments, part of iron was replaced with manganese during the preparation of the hydroxide. In more recent experiments, we have used commercially procured nano-crystalline iron oxide powder as the starting material.

B. **Extrusion**

ECAE experiments were performed at the Army Research Laboratory, Aberdeen by Dr. Laszlo Kecskes and his staff member, Micah Gallagher. Their extrusion press is similar to what is shown in a Youtube presentation (www.Youtube.com/watch?v=P_XKhGfeDNs).

$Fe_{16}N_2$ powder samples were sealed under inert atmosphere into nickel metal containers. They were loaded into the extrusion press and heated to 100 and 150 ^oC. Once the sample stabilized at the target temperature, the sample was extruded. About eighteen such extrusions were performed on the samples. Two modes of extrusions, viz., (1): 4C and (2): 6C gave the most promising results.

After the samples cooled down to room temperatures, the $Fe_{16}N_2$ samples were harvested by machining, EDM and polishing the samples. In a few cases we have succeeded in obtaining cubes of $Fe_{16}N_2$ samples.

Bulk densities of these specimens were determined using Pycnometry in a toluene solution. The best density for an extruded sample is 5.91 g./cc, which is ~75% of the x-ray density for the $Fe_{16}N_2$ phase.

BH loop measurements on the extruded samples were performed using a Walker Hysteresisgraph (see below).

C. **Evaluation of Magnetic Properties**

Three different types of magnetic properties were determined on the powders as well as extruded specimens prepared in this research. Illustrative examples of these results are described in the following:

1. Open M-H loops of the powders were determined in a vibrating sample magnetometer at room temperature. About 30 mg. of the specimen was packed in a specially designed sample capsule. The sample was loaded into this capsule from the reactor without ever exposing it to air after the formation of the nitride in the reactor inside an argon glove box. Thus, we ensure that the specimen does not oxidize. Further, the sample was tightly packed so that the particles do not move physically in the presence of the applied magnetic field. The sample capsule was then loaded into the magnetometer. Measurements were made following the routine procedure prescribed for the VSM.

A four-quadrant M-H loop was then determined on all the samples following this protocol.
A standard sample of nickel was used as a reference.

A typical M-H loop of a powdered sample is shown in Figure 3. This sample is made from a co-precipitate of FeO.OH with the addition of 3 wt% Mn. The final composition, after reduction and nitriding contains nearly 83 wt% 16:2 phase (determined from an analysis of the TMA curve – see below). It is interesting to note that we have succeeded in making a number of powder

samples with magnetization of >200 emu/g. at an external field of ~16 kOe, a saturation magnetization above 240 emu/g. and coercivities of >1,000 Oe.

In more recent experiments, we have prepared nanocrystalline powder of $Fe_{16}N_2$ from commercially obtained nanocrystalline a-Fe powder. These specimens showed coercivities of ~2,300 Oe. An M-H loop of such a powder sample is shown in Figure 4. A typical high resolution TEM of this powder is shown in Figure 5; this was obtained on the specimen supplied by AMC by Dr. Larry Allard at ORNL under a program supported by ARPA-E.

2. Thermo-magnetic analysis was determined on the powders employing a combination of VSM and a Bitter magnet. The external magnetic field was ~300 Oe and the temperature of the specimen was increased from room temperature to about 800 ^{o}C. The sample was maintained under pure argon atmosphere to prevent oxidation of the specimen. For instance, Figure 6 shows the variation of magnetization versus temperature at an applied field of ~300 Oe.

We note that, at room temperature, the magnetization measured is very small. This is due to the fact that the applied filed (~300 Oe) is much lower than the anisotropy field (16,000 Oe) of the 16:2 phase. At temperatures slightly above 220 ^{o}C (Figure 6), the magnetization increases sharply. This transition shows up as a typical first-order phase transformation. We have attributed this change as due to a transformation from the $Fe_{16}N_2$ to a mixture of $Fe_{14}N$ and α-Fe. These two phases are cubic and thus the sample no longer has magnetic anisotropy. In earlier studies, we have verified the powder x-ray diffraction patterns of the powder before and after this phase transformation. This has been confirmed by several other researchers [For instance, see 9].

It is also interesting to note that the relative height of this change in magnetization (relative to the total height in the plot of M vs T) gives a reasonably good semi-quantitative percentage concentration of the $Fe_{16}N_2$ phase.

Thus, in summary, we have been successful in determining whether or not the $Fe_{16}N_2$ phase is present in a specimen (By the presence of the transition at ~240 ^{o}C) and if so to what degree (By the relative magnitude of this change). Such an analysis was carried out for all the powder samples as well as extruded specimens in this study.

3. Results obtained on the B-H loop measurements determined with a Hysteresisgraph unit are shown in Figures 7 and 8. A standard sample of nickel was used as a reference. This measurement is obtained in a closed-loop mode and therefore is not subject to any uncertainty (as is the case with an open loop M-H measurements made in a VSM, that is subject to demagnetization corrections). In some extrusions, we were successful in being able to obtain cubic specimens from the extruded samples using a diamond wheel. We have measured the B-H loops of such specimens along the three orthogonal directions, relative to the extrusion direction. An illustrative result of such a measurement is shown in Figure 8. The results are summarized in Table 1. It is clear from the results shown in this figure that under the extrusion conditions employed in this study, we were unable to obtain samples with magnetic texture. It is, however, possible that under different extrusion conditions, we may be able to prepare higher density samples that may show magnetic texture. This is an area worth pursuing in future.

IV. RESULTS AND CONCLUSIONS

1. The extrusion experiments on the $Fe_{16}N_2$ phase (containing 3 wt% Mn) showed that:

> Under the experimental conditions investigated thus far, the best density of the extruded specimens are about 75% of the X-ray density.
>
> Extrusions at temperatures up to ~150 ^{o}C do not result in appreciable changes in the magnetization (compared to the powder).
>
> Extrusions at a temperature of ~150 ^{o}C result in a change of ~200 Oe out of ~1,000 Oe in the intrinsic coercivity. However, we believe that if we start the extrusions with powders that exhibit higher coercivities (such as what we now have - ~2,300 Oe), we can compromise some losses in the coercivity and yet succeed in making good magnets.

2. The best saturation induction obtained on the extruded specimen is ~12.5 kG. This value will improve much higher if we succeed in improving the density.

3. We have performed very limited extrusions. We believe that there are many more variables we need to examine to improve the density and induce crystal and magnetic texture.

4. Towards the end of this Grant period, we now have performed more optimized experiments and have succeeded in obtaining nanocrystalline $Fe_{16}N_2$ powder. The high resolution TEM show that uniform particles of ~20 nm are formed under these experimental conditions. These results are highly reproducible.

5. We believe that further optimization of these extrusion experiments on these nanocrystalline powders may yield bulk magnets with energy products of ~20 MG Oe in isotropic magnets and >35 MG Oe in anisotropic magnets – provided we are able to induce texture (in the latter case).

6. Finally, we believe that extrusion is the best technique to obtain bulk magnets based on the $Fe_{16}N_2$ composition. Figure 9 shows the BH loops of (a) A shock-compacted magnet prepared at Georgia Tech, (b) Magnetically compacted bulk magnet prepared at IAP Research, Inc. and (c) Extruded bulk magnet prepared at the Army Research Laboratory. These three bulk magnets were prepared using the $Fe_{16}N_2$ powder specimens supplied by AMC.

An examination of the above figure (9) reveals that (a) The shock-compacted specimen resulted in the formation of pure Fe specimen; this is reflected in the low coercivity and high magnetization as well as the shape of the loop. (b) The magnetically compacted magnets result in the low bulk density of the specimen. This is clear from its low magnetization. However, the coercivity remained almost in-tact. (c) The extruded magnet resulted in a 75% dense specimen that showed a high magnetization and a reasonably good coercivity.

A summary of the extrusion conditions and results obtained on the extruded magnets is given in Table 1.

It is desirable to continue this research activity to:

(A) Move forward the basic research in these materials (For example, the nature of the magnetic coupling between iron and manganese atoms in the 16:2 phase, how to improve the thermal stability of the 16:2 phase (See Figure 6) and mechanism of coercivity in these types of magnets.

(B) To explore additional experimental conditions in the extrusion process to fabricate low-cost, high energy magnets of both isotropic and anisotropic nature.

(C) To retain U.S. Leadership in this emerging area of magnetic materials –not containing a rare earth metal - which is critical for scientific, technical and economic development of the United States of America. Although there is a temporary relief from the "Rare earth crisis", it is better to pursue this type of research and development. For instance, extruded Fe-N magnets could play a very significant role in fulfilling the demand for isotropic magnets with about 15-20 MG Oe that could serve as a bridge between cheap ceramic ferrite magnets (Maximum energy product of 3 to 5 MG Oe) and expensive bonded Neo magnets with about 15-20 MG Oe.

V. REFERENCES

1. K.H. Jack, 'The iron-nitrogen system: the preparation and the crystal structures of nitrogen-austenite (γ) and nitrogen-martensite (α'),' Proc. Roy. Soc. **A208**, 200 (1951).

2. T.K. Kim and M. Takehashi, Appl. Phys. Lett., **20**, 492 (1972).

3. Y. Sugita, K. Mitsuoka, M. Komuro, H. Hochia, Y. Kozono and M. Hanazono, 'Giant magnetic moment and other magnetic properties of epitaxially grown $Fe_{16}N_2$ single-crystal films', J. Appl. Phys., 70, 5977 (1991).

4. W. E. Wallace and M.Q. Huang, 'Enhanced Fe moment in nitrogen martensite and $Fe_{16}N_2$' J. Appl. Phys., **76**, 6648 (1994).

5. S.G. Sankar and Laszlo Kecskes, "Consolidation of exchange-coupled magnets using equal channel angle extrusion at low temperatures", Provisional Patent Application (2014).

6. S.G. Sankar, S. Simizu, B. Zande and R.T. Obermyer, "Iron nitride powder for use in magnetic, electromagnetic and microelectronic devices", U.S. Patent 8,535,634 (2013).

7. S.G. Sankar et al., Synthesis and magnetic properties of $Fe_{16}N_2$, Invited paper presented at the Rare Earth Workshop, October 2014.

8. Christopher Wehrenberg, Brian Zande, Satoru Simizu, R.T. Obermyer and S.G. Sankar, Shock Compression Response of α''- $Fe_{16}N_2$ nanoparticles, J. Appl. Phys., **111**, 083522 (2012).

9. Marc Widenmeyer, Thomas C. Hansen and Rainer Niewa, 'Formation and decomposition of metastable α"-$Fe_{16}N_2$ from in-situ powder neutron diffraction and thermal analysis, J. Anorg. Allg. Chem., **639**, 2851-59 (2013).

10. Shinpei Yamamoto, Ruwan Gallage, Yasunobu Ogata, Yoshihiro Kusano, Naoya Kobayashi, Tomoyuki Ogawa, Naoaki Hayashi, Kaori Kohara, Migaku Takahashi and Mikio Takano, Chem. Comm., **70**, 7671 (2013).

11. H. Hiraka, K. Ohoyama, Y. Ogata, R. Gallage, N. Kobayashi, M. Takahashi, B. Gillon, A. Gukasov K. Yamada, 'Polarized neutron-diffraction study of the microscopic magnetic structure in α"-$Fe_{16}N_2$ nanoparticles", Phys. Rev., **B90**, 134427 (2014).

VI. ACKNOWLEDGEMENTS

The author thanks Laszlo Kesckes, Army Research Laboratory, Aberdeen for making his ECAE facilities available to perform this work and to Mica Gallagher in performing these extrusions. The author has benefited immensely during his discussions with them. The author thanks Brian Zande, Richard Obermyer, Satoru Simizu and Arkady Margolin at the Advanced Materials Corporation, Pittsburgh in the powder preparation, magnetic characterization and very useful discussions. The author also acknowledges the results reported by Larry Allard Jr. (High Resolution Transmission Electron Microscopy), Lara-Edgar Curzio and by Mike Bardy (X-ray) on the samples supplied by the author. All of them are from Oak Ridge National Laboratory; this work was also supported by a different contract from ARPA-E.

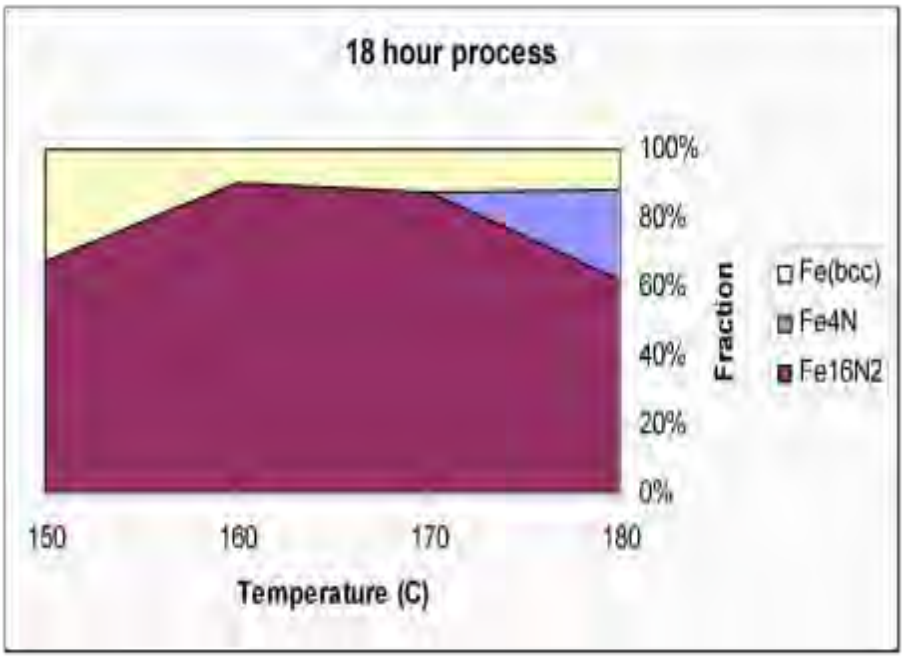

Figure 1 shows the fraction of the three phases, bcc Fe, Fe_4N and $Fe_{16}N_2$, depending on the process conditions.

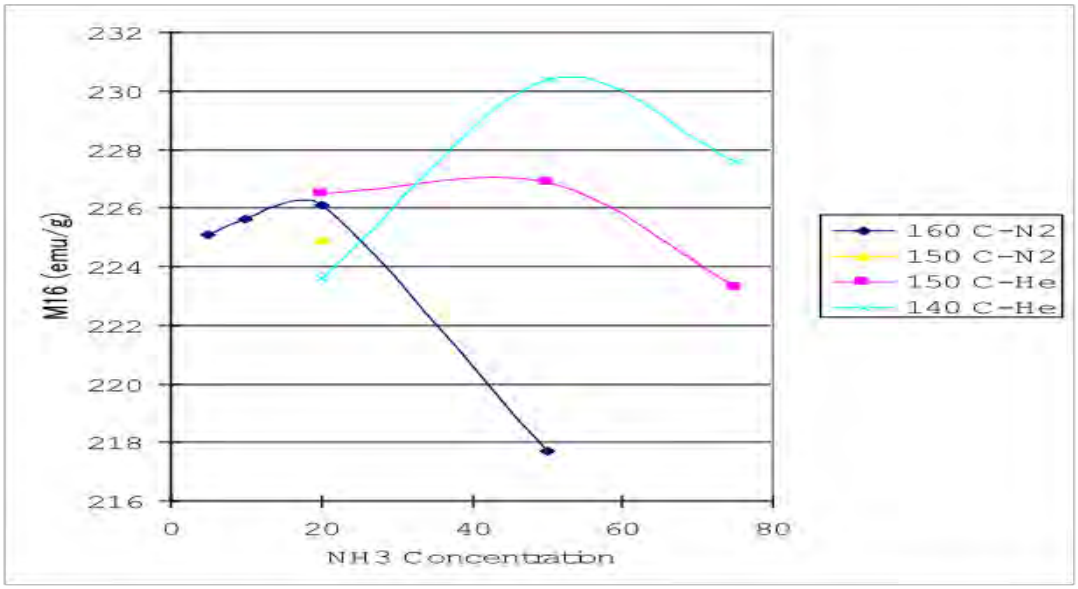

Figure 2. Magnetization (at an external magnetic field of ~16 kOe) of reaction products as a function of ammonia concentration in a mixture of ammonia and nitrogen at three different temperatures.

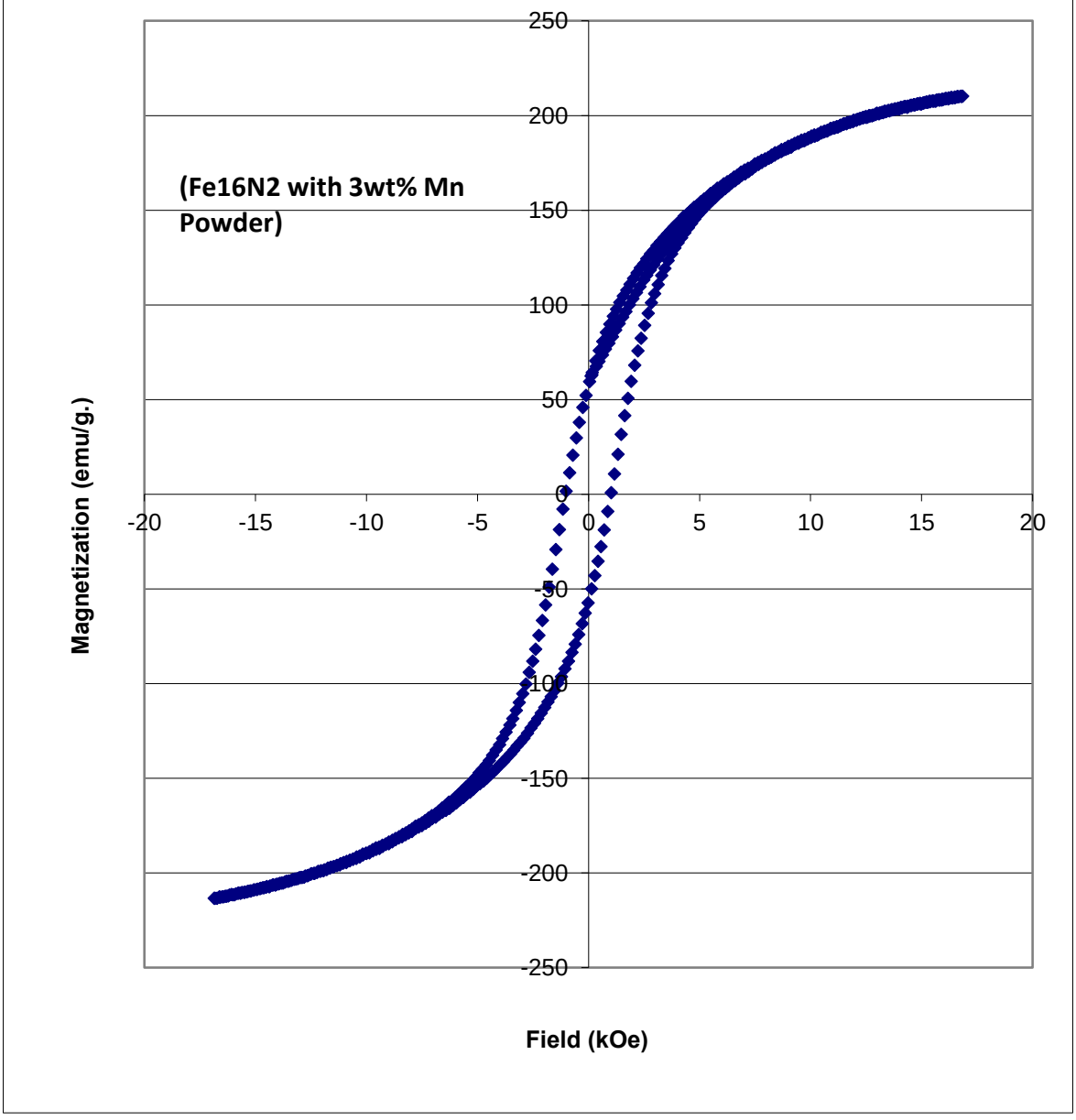

Figure 3. M-H loop of a $Fe_{16}N_2$ (with 3wt% Mn) powder. The magnetization at 16 k Oe is ~208 emu/g. The saturation magnetization is 240 emu/g. and the coercivity of this powder is ~1,000 Oe.

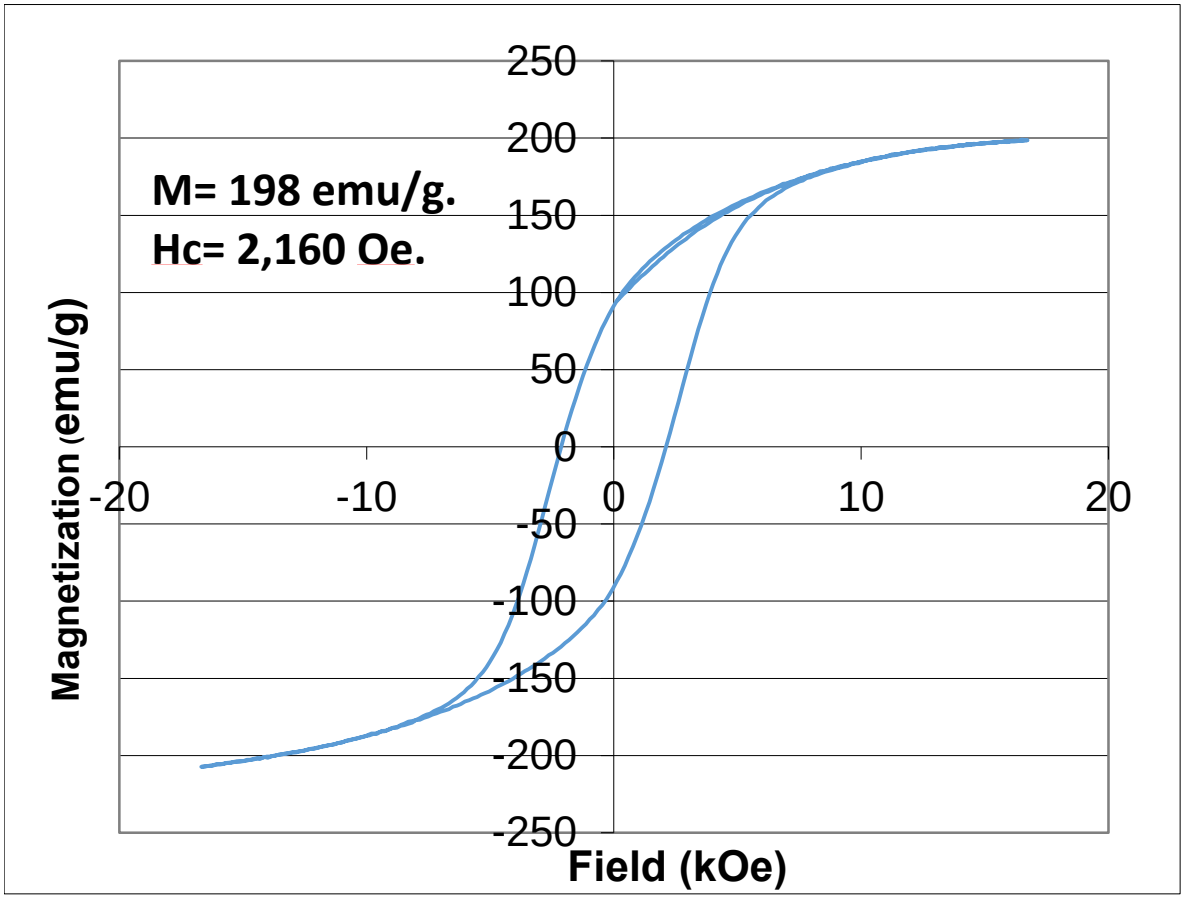

Figure 4. M-H loop of a $Fe_{16}N_2$ powder prepared from nanocrystalline commercially procured Fe_2O_3. This sample exhibits a magnetization of 198 emu/g at an external field of 16 k Oe, a saturation magnetization of 245 emu/g. and a coercivity of 2,160 Oe. The high resolution TEM of this powder is shown in Figure 5.

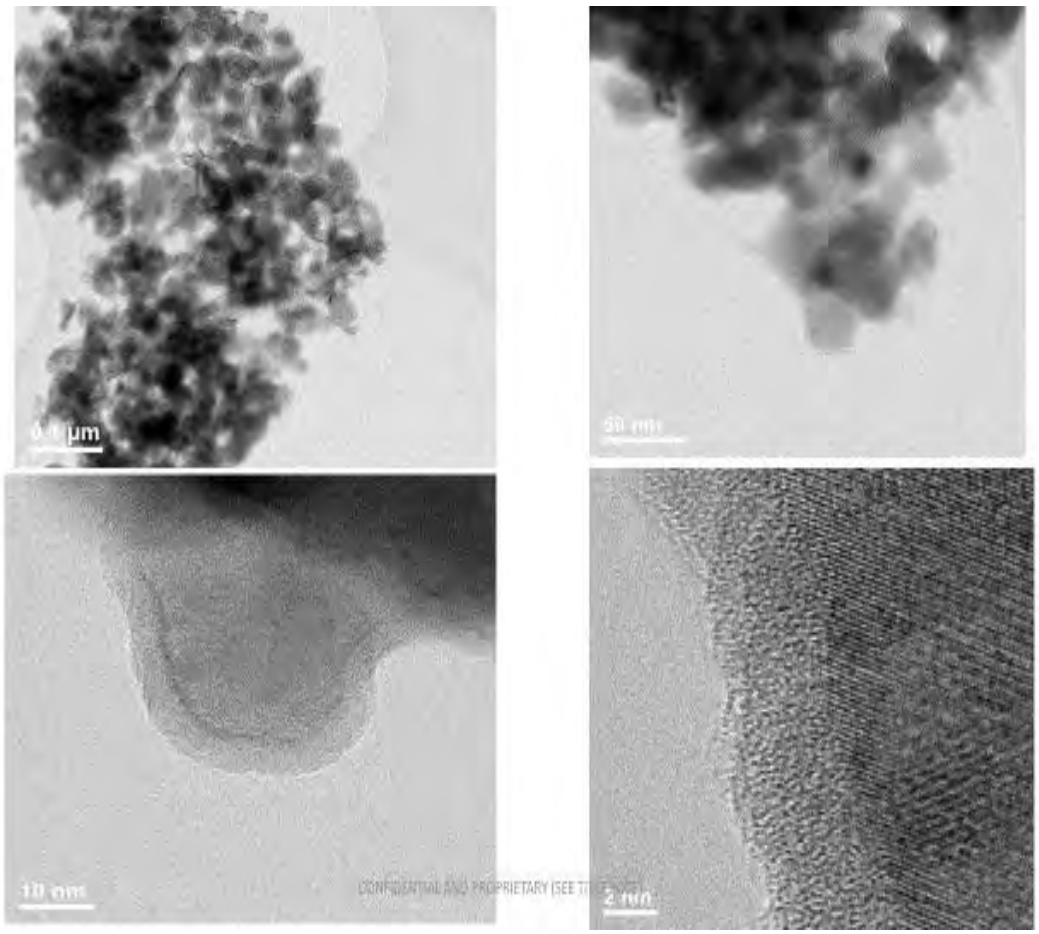

Figure 5. High resolution TEM of the $Fe_{16}N_2$ powder made from commercial nanocrystalline Fe_2O_3 powder. Top left shows a number of particles; Top right shows the size of a particle to be about 20 nm; Bottom left shows the surface coated with an iron oxide layer of about 2 nm thickness (used for passivation purposes) and bottom right shows the lattice spacings confirming that the particles are of $Fe_{16}N_2$ composition (Courtesy: Lawrance Allard, ORNL).

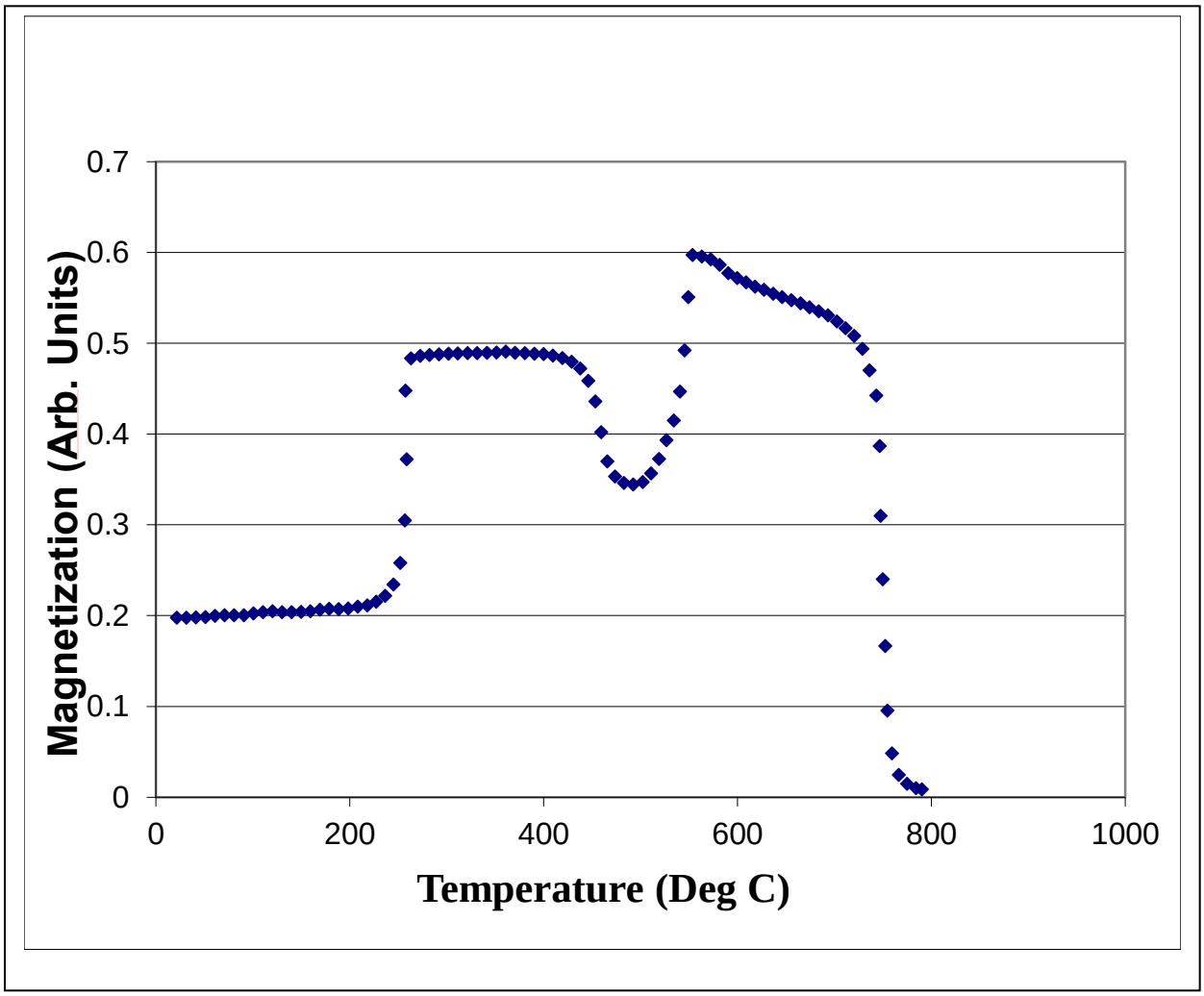

Fig. 6 Thermomagnetic Analysis of $Fe_{16}N_2$ Powder performed at low applied magnetic field (~300 Oe.). $Fe_{16}N_2$ rearranges to Fe_4N + Fe at a temperature of about 240 deg C.

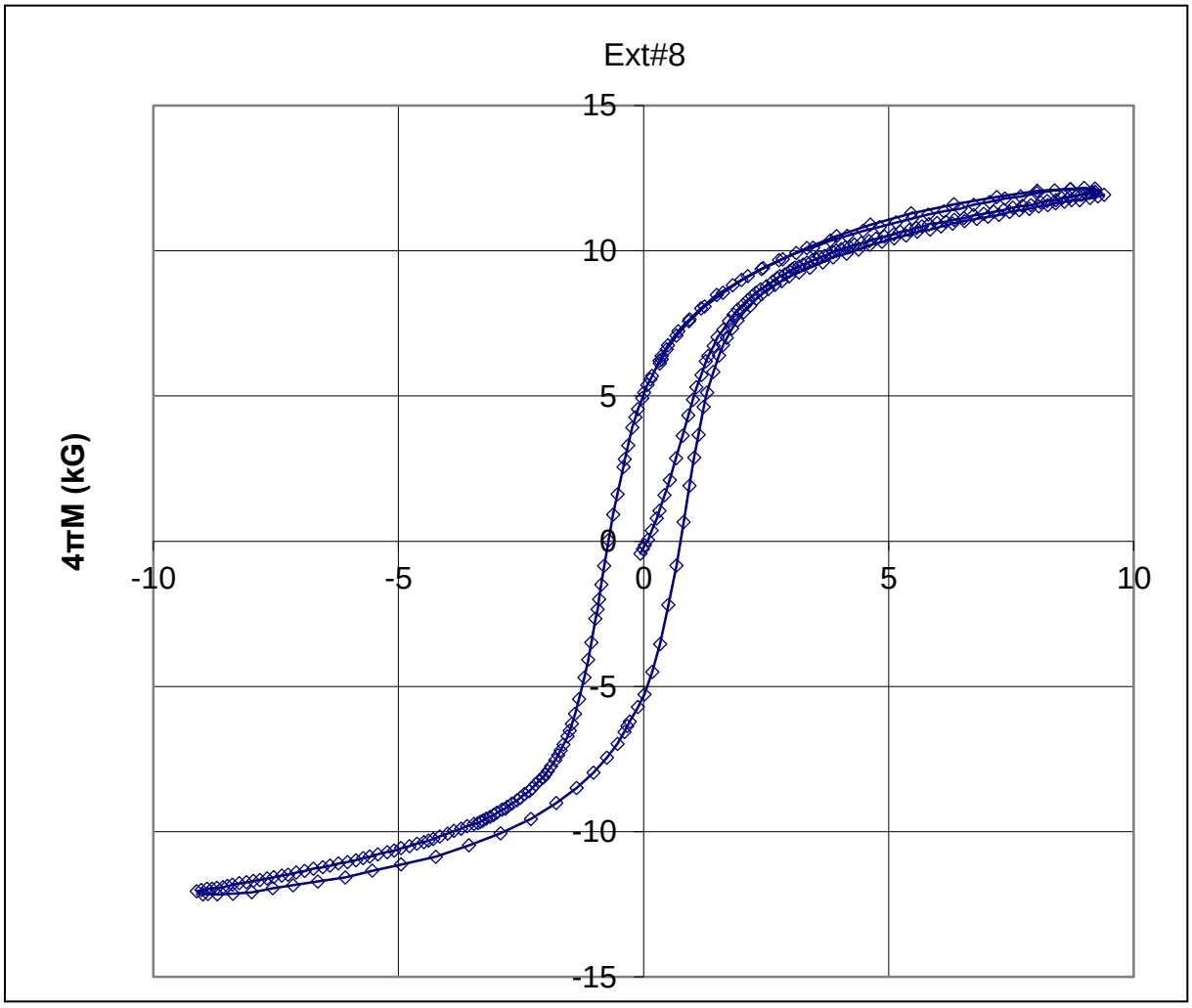

Figure 7. B-H loop of an extruded sample (Sample Number 8) from $Fe_{16}N_2$ (with 3wt% Mn) powder. This sample exhibits the highest value of maximum induction of 12 kG. The remanence of this sample is ~5 kG and its coercivity is ~800 Oe. The density of this sample measured using pycnometry is 5.41 g./cc which is about 73% of the X-ray density

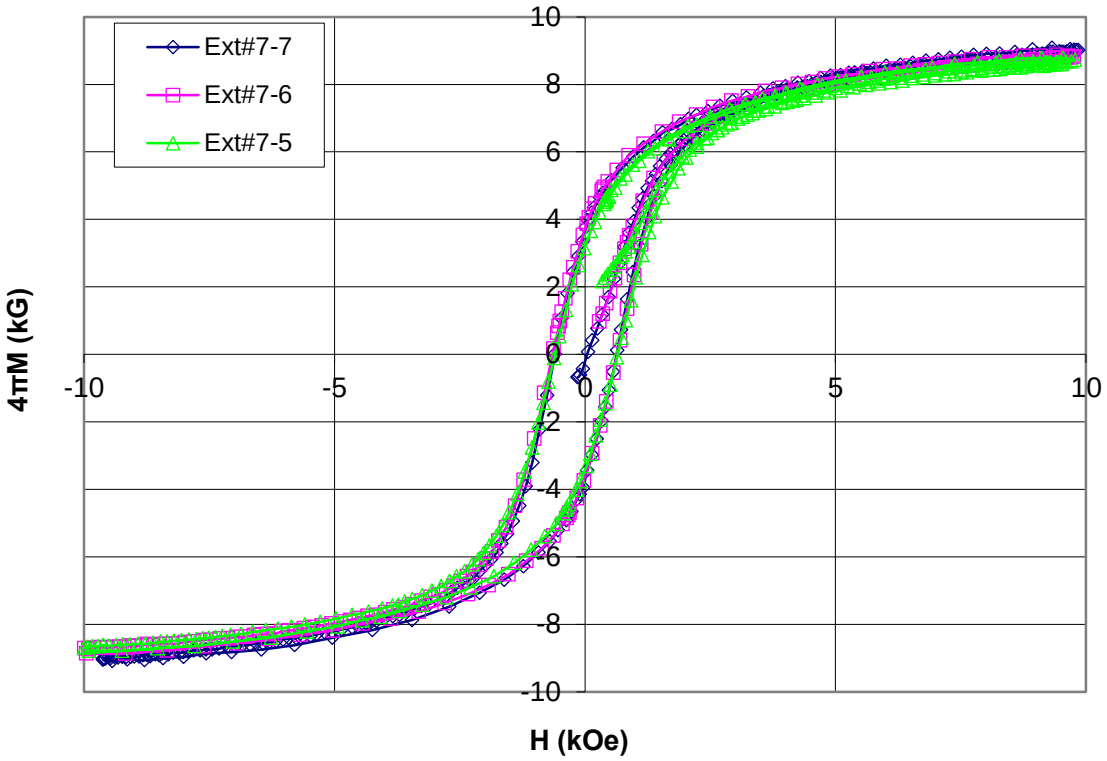

Figure 8. B-H loops of an extruded sample (Extrusion Number 7) from Fe16N2 (with 3wt% Mn) powder. Loops are shown for three directions indicating the lack of texture.

Sample	Extrn Conditions	Density	Composition of	4πMmax	Br	Hc
		g./cc	the $Fe_{16}N_2$ phase	(kG)	(kG)	(kOe)
Ext#7-5	4C at 150 deg C	4.85	65.3%	8.78	3.18	0.62
Ext#7-6	4C at 150 deg C			8.87	3.51	0.64
Ext#7-7	4C at 150 deg C			9.09	3.55	0.61
Ext#8	4C at 100 deg C	5.41	72.8%	12.16	5.04	0.72
Ext#9-7	6C at 150 deg C	5.27	70.9%	10.37	3.18	0.41
Ext#10	8C at 100 deg C	5.08	68.4%	11.14	4.93	0.62
Powder			83%	210 emu/g		~1.0

TABLE 1. Extrusion conditions and bulk density, estimated concentration of the $Fe_{16}N_2$ phase, Induction, remanence and coercivity of the extruded samples 7 (along three directions), 8, 9 and 10 are listed. For comparison, results on the powder sample are also shown. All the extrusions were performed on the same batch of powders.

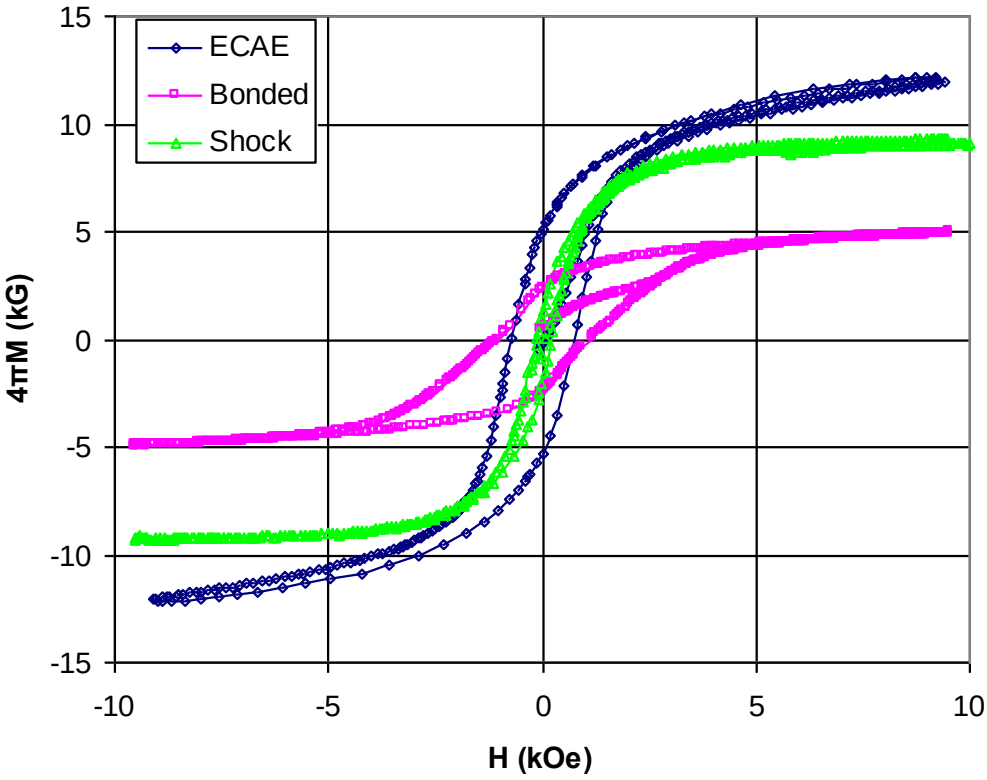

Figure 9. Hysteresis loops obtained for the permanent magnets prepared by three different methods.